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Principles of Adsorption of Organics at Solid-Solution Interfaces

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ABSTRACT

General thermodynamic and molecular approaches to an understanding of organic adsorption at solid-solution interfaces are proposed. Particular importance is attached to the nature of surface sites on the solid and on the nature of functional groups on the organic. It is shown that such a systematic treatment can account for adsorption of small organics, larger surfactant molecules and ions, and polymers at many solid-solution interfaces.

INTRODUCTION

A large number of heterogeneous systems and processes in nature and in science and technology are controlled to a significant extent by the presence or addition of organic solutes which concentrate at the surfaces of the solids dispersed in the liquid phase. The process may require that the colloidal solid particles stay dispersed rather than aggregated, or it may depend on aggregation or coagulation of some or

all particles in the system. To these ends, small organic nonionic solutes, ionic and nonionic detergents or surfactants, and large polymer or polyelectrolyte molecules are present or are added to control the state of dispersion as required.

The aim of the present paper is to examine the nature of the adsorption of organics at solid-liquid interfaces with the view to formulating general principles that can be used in many different systems where colloid stability or instability is required for successful operation of the process.

The solids one may encounter are many and varied, but they can be classified into two broad categories of inorganic and organic. Examples of these are shown in Table 1. In general, this paper is concerned with aqueous colloidal dispersions; analysis of nonaqueous dispersions is considered elsewhere [1].

TABLE 1. Important Colloidal Dispersions

Solids	Examples	Processes/uses
(A) Inorganics		
Metal powders	Ni, Ge, Fe	Catalysts, devices, tapes
"Metal" oxides	TiO ₂ , SiO ₂ , ZnO	Paint pigments, pharmaceutical fillers
Silicates/alumino-silicates	Kaolin, asbestos	Catalyst supports, glass manufacture, ceramics
Metal sulfides	ZnS, PbS, CuFeS ₂	Phosphors, froth flotation, pigments
Carbonates, sulfates	CaCO ₃ , BaSO ₄	Fillers, pharmaceuticals, brighteners
(B) Organics		
Carbon	C, carbon black, active carbon	Synthetic rubber, printing ink, adsorbents, fillers
Latex particles	Styrene, butadiene, polystyrene	Paints, papers
Natural products	Wood pulp, wool, blood	Paper manufacture, fibers
Pharmaceuticals, dyes	Phenacetin	Drugs, medications, dyeing

Fortunately, the solids of Table 1, when considered as aqueous colloidal dispersions, all respond in a fundamental way to a single or characteristic variable; their electrical surface properties are controlled by pH in that H^+ and OH^- ions are responsible for charging or discharging the groups or sites on their surfaces. These groups may be $-COOH$ or $-NH_2$ on biocolloids, $-SO_3H$ group on latex particles, surface hydroxyls on oxides and silicates or oxidized layers on metal or metal sulfide particles, and S^{2-} , CO_3^{2-} , SO_4^{2-} , or M^{n+} groups on sulfides, carbonates, and sulfates. The relative population of protonated, neutral, or negative groups on the particle, surface is controlled by the solution pH, and the electrostatic potential difference across the solid-aqueous solution interface (ψ_0) is given by Nernst-type equations of the form

$$\psi_0 = \frac{RT}{F} \ln \frac{a_{H^+}}{a_{H^+}^\circ} + f(K', K'') \quad (1)$$

where R is the gas constant, T is the absolute temperature, F is the Faraday, a_{H^+} and $a_{H^+}^\circ$ are the activities of H^+ in solution at any surface charge condition (a_{H^+}) or at a reference state of zero surface charge ($a_{H^+}^\circ$), respectively, and K' and K'' are the acid dissociation constants for addition and removal of protons, respectively, from ionizable sites in the interface.

The unifying role of pH, established for many natural and synthetic systems [2, 3], allows great simplification in considering the fundamental principles of adsorption.

There are almost as many variations as shown in Table 1 when one considers the kinds of organic additives in use or found in natural and technological processes. Some simplification is possible as shown in Table 2 if the organics are considered under headings of small, medium, or large molecules. All molecular species that concentrate at interfaces to control the state of the colloidal dispersion are dipoles at least, many being ionic. It is for this reason that adsorption of organics at solid-aqueous solution interfaces is seen in large part in electrostatic terms.

Before considering the molecular interactions important in adsorption of organics at solid-aqueous solution interfaces, it is important to establish a thermodynamic description of the process of adsorption. First, if one can establish experimentally that a given organic does adsorb, i.e., has a positive surface excess, then the process of adsorption has lowered the surface free energy of the solid-aqueous interface. The corollary to this (viz., that since the

TABLE 2. Organic Additives to Colloidal Dispersions

	Examples	Uses
A. Small organics	Short chain alcohols, chlorinated hydrocarbons, alkylamines, hydrazines, oximes, hydroxamates	Dispersants, sizing agents, foam stabilizers
B. Surfactants	Lauryl sulfate, alkylbenzene sulfonates, long chain alcohol-ethylene oxide condensates	Detergency, flotation, wetting, adhesion preparations
C. Low molecular weight polymers	Carboxymethylcellulose, polyethylene oxides	Dispersants, wetting agents, coagulants
D. High molecular weight polymers	Polyacrylamide, polyvinyl pyrimidine	Flocculants, stabilizers, grouting agents, pelletizing additives

solid with adsorbed organic will have a lower energy than the solid in contact with the aqueous solution and therefore the organic will adsorb positively) is true in almost all cases simply because of the unique properties of water. Thus organic liquids have, except for some very exotic possibilities, lower liquid-vapor interfacial free energies than water. Similarly, almost all solid-organic liquid interfacial free energies are lower than those for solid-water interfaces.

THE SOLID-WATER INTERFACE

The unique role of H^+ and OH^- ions in controlling the fundamental properties of solid-water, or strictly, solid-aqueous electrolyte interfaces, is conveniently represented as equilibria between positive ($-XH_2^+$), neutral ($-XH$), and negative ($-X^-$) sites at the interface, thus



for which

$$\alpha_+ K' = \alpha_0 a_{H^+} \quad (2)$$

and



for which

$$\alpha_0 K'' = \alpha_- a_{H^+} \quad (4)$$

where α_+ , α_0 , and α_- are the fractions of positive, neutral, and negative sites at the surface, respectively. By definition,

$$\alpha_+ + \alpha_0 + \alpha_- = 1 \quad (5)$$

and in terms of ionic or charged sites only, then

$$K_S = (K'K'')^{-1} = (\alpha_+/\alpha_-)(a_{H^+})^{-2} \quad (6)$$

where K_S is the "surface equilibrium constant." If the activity of protons in solution is adjusted to a value of $a_{H^+}^0$ for which the number of positive sites equals the number of negative sites, then $(\alpha_+/\alpha_-) = 1$, and

$$K_S = (a_{H^+}^0)^{-2} \quad (7)$$

This condition is referred to as the point of zero charge (pzc) or in the presence of simple electrolytes only, is identical to the isoelectric point (iep). Some selected pzc/iep values are shown in Table 3, all expressed in terms of pH.

TABLE 3. Point of Zero Charge (pzc) or Isoelectric Points (iep) of Several Solid-Aqueous Solution Interfaces

Solid	pzc/iep (pH)
SiO ₂ (crystalline)	2.5-3.0
SiO ₂ (amorphous)	1.5-2.0
TiO ₂ (rutile)	5.8
Al ₂ O ₃ (corundum)	9.1
Al ₂ O ₃ (γ -alumina)	8.8
Sulfonated latex	0.0-0.5
Bovine serum albumin	5.1
Kaolinite	3.8
ZnS	8.0
Active carbon	~1.0
Platinum black	0.5-1.2
Crystalline cellulose	2-4
Bacteriophage T. 3	7.2

The pzc or iep values can be obtained by many methods [2] including direct titration, coagulation rate studies, and from electrokinetic or zeta potential methods.

The important consequence of knowing a pzc or iep value is that at pH values below it, the surface has a net positive charge, and at pH values above it, the surface has a net negative charge.

The acid-base surface equilibria illustrated in Eqs. (1) and (2) are able to generate these negative, neutral, and positive sites as a function of pH with the net charge being controlled by pH and K' and K'' , the surface acidity constants. Thus, as shown in Fig. 1, we can

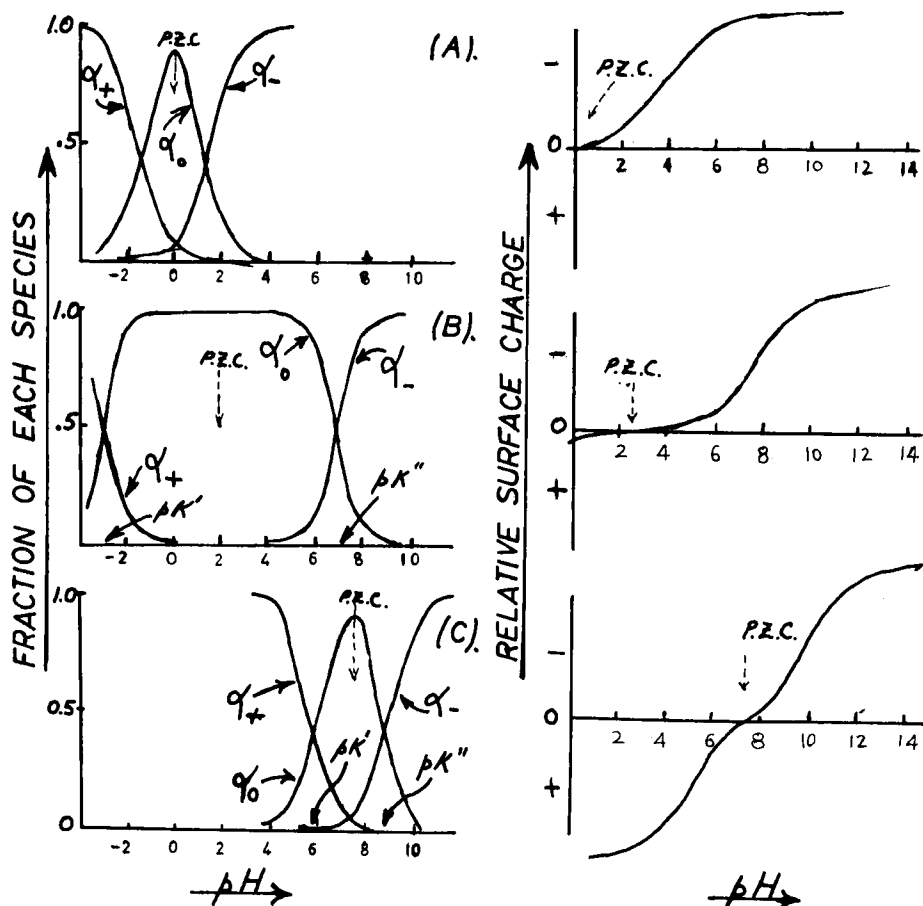


FIG. 1. Schematic representation of the variation with pH of surface site distributions and relative surface charges for (A) a strong acid system, e.g., sulfonated latex; (B) a strong acid/weak acid system, e.g., SiO_2 ; and (C) a weak acid/weak acid system, e.g., Fe_2O_3 or TiO_2 .

imagine three surfaces A, B, and C which will yield different charge densities at any given pH. These are meant to represent, in a general way, a sulfonated latex (A), SiO_2 (B), and Fe_2O_3 (C). The sulfonated latex has a strong monoprotic acid at its surface ($-\text{SO}_3\text{H} \rightarrow -\text{SO}_3^-$), silica has a weak monoprotic acid at its surface ($-\text{SiOH} \rightarrow -\text{SiO}^-$), and Fe_2O_3 has a weak diprotic acid at its surface ($-\text{FeOH}_2^+ \rightarrow -\text{FeOH} \rightarrow -\text{FeO}^-$).

Thus a sulfonated latex has a uniformly negative surface over most of the normal pH range as does SiO_2 , except that for SiO_2 the surface charge increases only slightly between pH 2 and pH 6. Fe_2O_3 has the possibility of positive or negative surface charge, the magnitude of which increases sharply on either side of the pzc.

The above consideration of surfaces of various kinds in terms of "charge" has an analogous formulation in terms of "potential." Since the surface charge must, to preserve electroneutrality in the system, be balanced by an equal but opposite charge on the solution side of the interface, an electrical double layer (edl) is considered to form at the interface. Various models of the edl at solid-aqueous interfaces have been proposed and are reviewed in standard texts. For organic adsorption the most useful is one of the Stern double-layer models depicted schematically in Fig. 2. The major features of this model are:

1. The surface charge (σ_0) is due to dissociation of acid/base groups on the surface.
2. The total double-layer potential (ψ_0) due to this charge is given by a Nernst-type relationship such as Eq. (1).
3. Organic ions (and molecules), if specifically adsorbed, approach to the Stern plane distance δ out from the surface to yield a charge σ_δ and a potential ψ_δ .
4. The diffuse layer begins at this plane δ and is characterized by a potential $\psi_d = \psi_\delta$ which decays exponentially to zero at the limit of the diffuse layer.
5. The "thickness" of diffuse layer is given by $1/\kappa$ where ψ_d falls to (ψ_d/e) , where e is the base of Natural logarithms at a distance of $1/\kappa$ out from the plane δ .
6. The shear plane or the plane which gives rise to the electrokinetic or zeta potential occurs at the beginning of or slightly into the diffuse layer.

GENERAL ADSORPTION CONSIDERATIONS

The total free energy of adsorption of species ranging from simple small organic ions and molecules all the way to complex polyelectrolytes

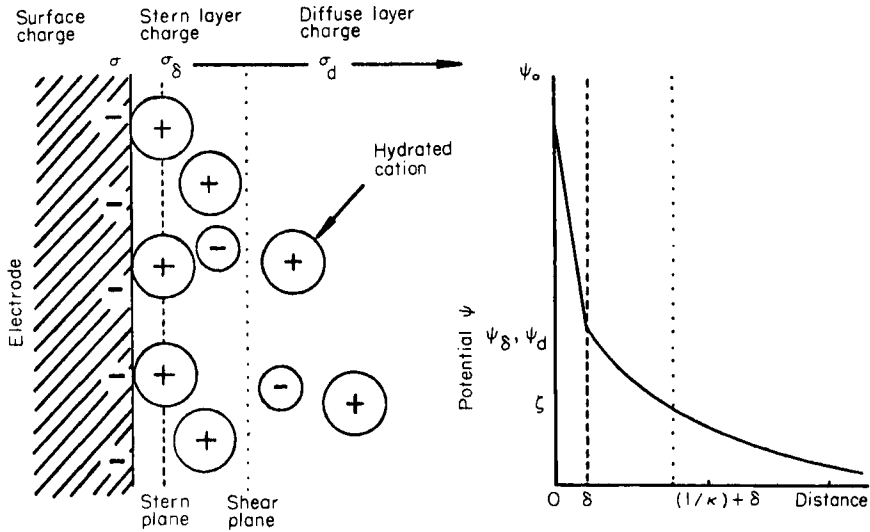


FIG. 2. General structure of the Stern model of the electrical double layer at solid-solution interfaces showing the Stern plane of adsorbed ions and the plane of shear at which the zeta-potential is measured.

must of necessity be broken down into component parts, viz.,

$$\Delta G_{\text{ads}}^{\circ} = \sum_j \Delta G_j^{\circ} \quad (8)$$

where ΔG_j° may be contributions to adsorption identifiable as separate independent processes. Following an earlier treatment [2], Eq. (8) may be given by

$$\Delta G_{\text{ads}}^{\circ} = \Delta G_{\text{elec}}^{\circ} + \Delta G_{\text{solv}}^{\circ} + \Delta G_{\text{hb}}^{\circ} + \Delta G_{\text{vdw}}^{\circ} + \Delta G_{\text{chem}}^{\circ} \quad (9)$$

where $\Delta G_{\text{elec}}^{\circ}$ is the +, -, or coulombic free energy change and is given by $z_{\pm} e \psi_0$. $\Delta G_{\text{elec}}^{\circ}$ is negative when the adsorbing ion is opposite in sign to the sign of the net surface charge. Thus referring to Fig. 1, cation adsorption is in coulombic terms spontaneous above the pH of the pzc while anion adsorption is spontaneous below the pH of the pzc.

The potential ψ_δ is the electrostatic potential at a plane distance δ out from the surface, and it is at this plane where the particular ion adsorbs. If the adsorbing species were a dipole, then $\Delta G_{\text{elec}}^\circ$ in such a case is always negative and is given by the product of the electric field at the interface and the dipole moment.

The second term in Eq. (9) is the change in free energy of the hydration sphere of an ion as it adsorbs and becomes partly desolvated in the process. For adsorption on insulators this $\Delta G_{\text{solv}}^\circ$ term is always positive but can be near zero or slightly negative for adsorption of ions on a semiconducting solid, such as TiO_2 , which has a dielectric constant of the same order of magnitude as that of water. $\Delta G_{\text{solv}}^\circ$ is negative for ion adsorption at metal-electrolyte interfaces.

The third and fourth terms will be considered in more detail in subsequent sections. It is sufficient at this stage to identify them as contributions to adsorption due to hydrophobic interactions [4] ($\Delta G_{\text{hb}}^\circ$) and London dispersion of Van der Waals interactions ($\Delta G_{\text{vdw}}^\circ$). The final term $\Delta G_{\text{chem}}^\circ$ includes specific "chemical" interactions ranging from hydrogen bonding to covalent bonding. (In an earlier attempt [1] to quantify organic-adsorbent interactions, hydrogen bonding was separated out of $\Delta G_{\text{chem}}^\circ$ and hydrophobic interactions were included in the Van der Waals term. The present separation has proved more useful.)

This method of analysis of data on the adsorption of organics at a mineral-water interface is illustrated by reference to the data of Fig. 3. The system is sodium dodecyl sulfonate adsorbing at the alumina-aqueous electrolyte interface [5]. Shown as a function of the equilibrium concentration of the surfactant is the adsorption density, the zeta potential of the alumina colloid, and the change in wettability of the alumina. The wettability is directly related to the work of adhesion (W_A) and the contact angle (θ) at the alumina-water-air interfaces as

$$W_A = (1 + \cos \theta) \gamma_{\text{AW}}$$

where γ_{AW} is the air-water interfacial tension and θ is measured through the water phase. The initial rise in adsorption density is paralleled by no change in zeta potential, indicating that surfactant ions are exchanging in the diffuse layer and are not entering the Stern plane. Then at a particular concentration termed the "hemimicelle concentration" (HMC), the adsorption and the magnitude of the zeta potential both increase sharply; there is also a sharp increase in the contact angle. Adsorption eventually reduces the zeta

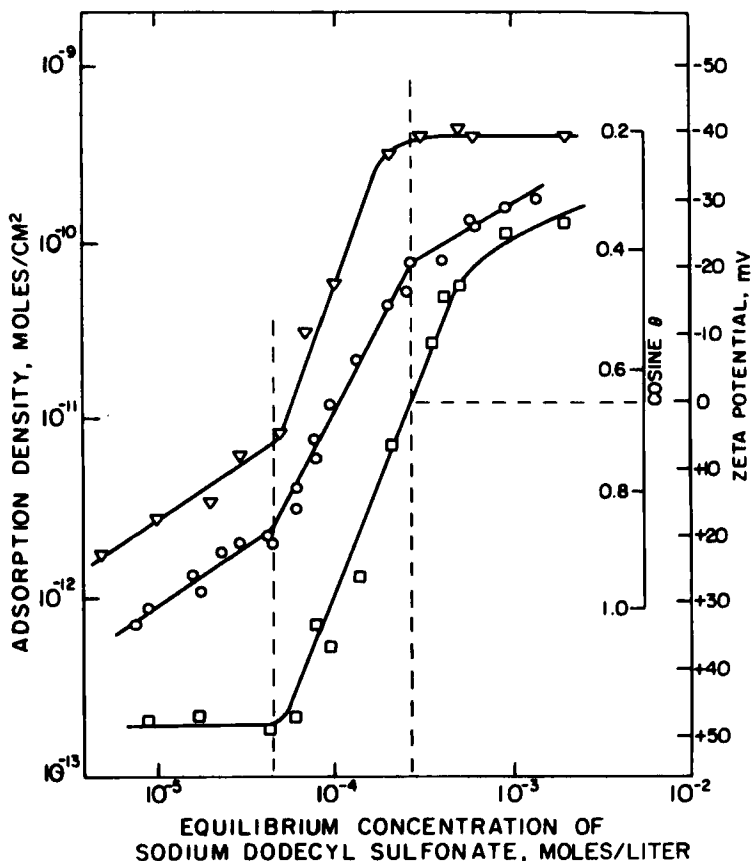


FIG. 3. The adsorption density of sodium dodecyl sulfate on alumina, the zeta-potential of alumina, and the contact angle on alumina as a function of the equilibrium concentration of surfactant at pH 7.2 and ionic strength 2×10^{-3} M at 25°C. (∇) Contact angle. (\circ) Adsorption density. (\square) Zeta potential. (From Ref. 2 with permission.)

potential to zero, and the adsorption density continues at a less marked rate of increase.

If the marked increase in adsorption at the HMC is identified as the onset of hydrophobic interactions (ΔG_{hb}°), then at zero zeta potential

$$\Delta G_{ads}^{\circ} = \Delta G_{hb}^{\circ}$$

If hydrophobic effects are considered as the product of the number of $-\text{CH}_2-$ groups in the chain (n) times a hydrophobic energy per CH_2 group (ϕ_{hm}), then at zero zeta potential

$$\Delta G_{\text{ads}}^{\circ} = n\phi_{\text{hm}}$$

Since

$$\Delta G_{\text{ads}}^{\circ} = -RT \ln K_{\text{ads}}$$

where K_{ads} is the adsorption equilibrium constant. Then from the Stern model of the electrical double-layer

$$RT \ln [\Gamma_0 / (2rC_0)] = n\phi_{\text{hm}}$$

where Γ_0 and C_0 are the adsorption densities and equilibrium concentration at zero zeta potential, respectively, and r is a constant; the adsorption density at zero zeta potential is constant at constant pH and supporting electrolyte concentration for an homologous series of surfactants. Thus if $\ln C_0$ is plotted as a function of n , a straight line results, the slope of which yields ϕ_{hm} , the hydrophobic contribution per CH_2 group to the total free energy of adsorption.

In seeking a general understanding of the relation between the structure of an organic and its adsorption properties, it is found that one can separate out hydrophilic functions from hydrophobic functions. Examples of hydrophilic centers are polar head groups, double bonds, and ether linkages, while examples of hydrophobic functions include methyl and methylene groups and aromatic or heterocyclic centers.

For the process of transferring a polar group out of water to an interface, the free energy change is positive and must be recovered by, say, a negative electrostatic free energy ($\Delta G_{\text{elec}}^{\circ}$) of interaction with the charged surface. In contrast, the system will lower its free energy when hydrophobic centers are removed from water into a hydrophobic environment. Such a hydrophobic environment is provided by a micelle interior, a hemi-micelle of adsorbed organics at a solid-liquid interface, by hydrocarbon-water solutions, or by hydrocarbon liquid.

Considerable advance has been made recently by Lin and Somasundaran [6] who summarized many of these hydrophobic group free energy changes. They considered the measured changes in solubility, micelle formation, and adsorption of many organics as a function of the alkyl chain length of the organic. The known linearity

AQUEOUS SOLUTION

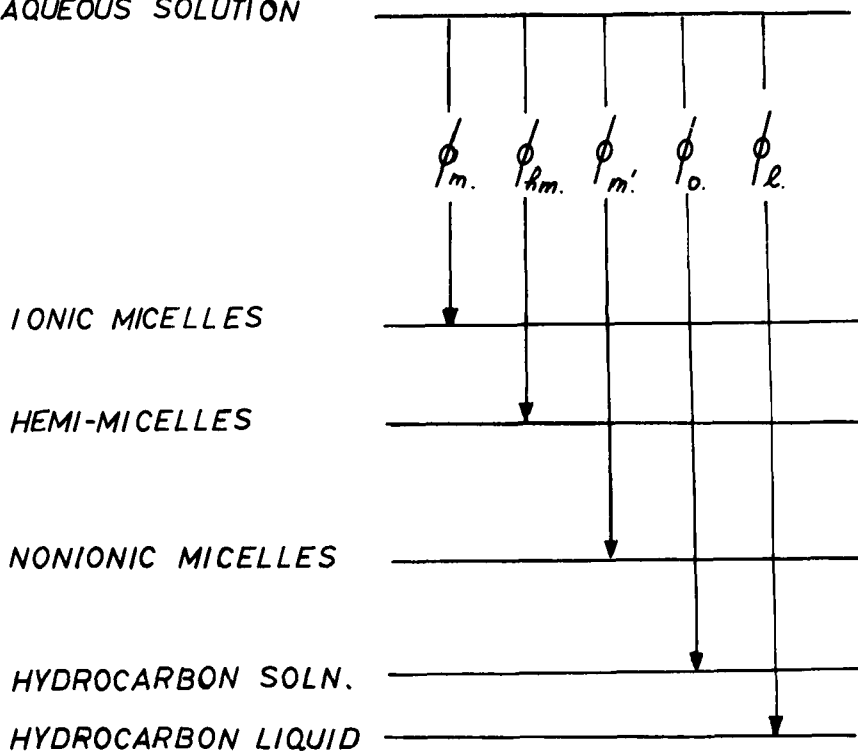


FIG. 4. Schematic representation of the hydrophobic contributions per CH_2 group to the lowering of the total free energy change in processes where alkyl surfactants are involved (after Lin and Somasundaran [6]).

of $\log(\text{property})$ vs chain length (n) yields a hydrophobic free energy [ϕ , equivalent to $(\Delta G_{\text{hb}}^\circ/n)$ of Eq. 9] that is a free energy change per $-\text{CH}_2-$ group. Data selected from their study is summarized in Table 4 and Fig. 4. The energy unit is shown as kT , where k is the Boltzman constant and T the absolute temperature. At 25°C , $1 kT$ is approximately 600 cal/mole .

It can be seen that the system will gain increasing amounts of energy as a CH_2 group is transferred from the aqueous solution to an ionic micelle, a hemi-micelle or adsorbed layer at the solid-solution interface, a nonionic micelle, an aqueous hydrocarbon solution, and finally a hydrocarbon liquid. Smaller, but still significant lowering of

TABLE 4. Free Energy Changes per CH₂ Group for Various Transfer Processes Involving Organics

Transfer of alkyl chains		Organic reagents	Total free energy change per CH ₂ group
From	To		
Aqueous solution	Ionic micelles	Fatty acid soaps, alkyl sulfates, alkylammonium and trimethyl ammonium halides	$\phi_m = -0.61$ to -0.69 kT
Aqueous solution	Hemi-micelles at S-L interface	Alkylammonium acetates, alkylammonium sulfonates	$\phi_{hm} = -0.71$ to -0.98 kT
Aqueous solution	Nonionic micelles	Oxyethylene hydrocarbons	$\phi_m' = -1.10$ to 1.22 kT
Aqueous solution	Hydrocarbon solution	Long chain (n = 8 - 16) fatty acids	$\phi_o = -1.39$ kT
Aqueous solution	Hydrocarbon liquid	alcohols (n = 4 - 10), octane, alkyl amines (n = 10 - 14)	$\phi_l = -1.34$ to -1.39 kT $\phi_l = -1.17$ kT $\phi_l = -1.53$ kT

the free energy of systems will occur by transfer from micelles to adsorbed layers (hemi-micelles) or to hydrocarbon solution and liquid phases.

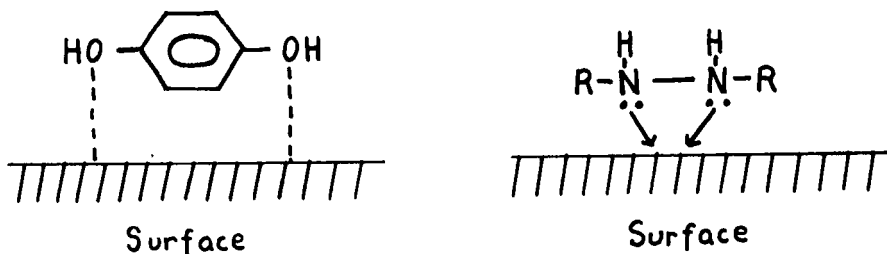
PARTICULAR ADSORPTION PROCESSES

Small Organics

The nature of the adsorption of small organic molecules, the upper level of size of which we shall arbitrarily set as a 8 to 10 carbon fatty acid, for example, has received very little attention. The hydrophilic-hydrophobic balance in such molecules is often small, so that the ΔG_{hb}° term of Eq. (9) is also small. Again, if they are dipoles rather than ions, the electrostatic term ΔG_{elec}° is likewise small. The desolvation term, except for very small organics, will also be negligibly small.

It appears that the dominant terms in their adsorption are ($\Delta G_{\text{chem}}^{\circ} + \Delta G_{\text{hb}}^{\circ}$).

Many of the small organics used are thought to be hydrogen bonded or to be weakly coordinately bound to sites on the surface. Examples of such interactions, the energies of which appear in $\Delta G_{\text{chem}}^{\circ}$, are



Here a hydrogen bond is formed between the O of the phenolic hydroxyl and, say, the H of a surface hydroxyl or from the H of the phenolic hydroxyl to the O of surface hydroxyls. Since aqueous solid-liquid interfaces are extremely difficult to study in situ by conventional IR and Raman spectroscopy, this obvious spectroscopic technique is of little value. Some significant advances may come from the multiple attenuated total reflectance method as described by Weber [7].

Actual coordinate binding of lone pairs on nitrogen, oxygen, and sulfur centers in small organics does seem more important in many cases than a hydrogen bonding interaction. Unfortunately, there are very few systematic studies of one such organic on surfaces of different electrophilic character or of several related increasingly nucleophilic molecules on the same surface. It would appear opportune to apply the Hammett or similar treatments to the adsorption of small organics.

Surfactants

The mechanism of adsorption of long-chain surfactants was considered in a previous section. The breakdown of the total free energy of adsorption as shown in Eq. (9) has been most successful in the case of the adsorption on oxides and clays of alkylammonium, alkylsulfonate and sulfate, alkylarylsulfonate, and fatty acid adsorption. With the exception of the fatty acids, adsorption is due to

$$(\Delta G_{\text{elec}}^{\circ} + \Delta G_{\text{hb}}^{\circ})$$

As soon as the plus-minus interaction locates a partial (usually 1/100) monolayer, the ΔG_{hb}° term becomes increasingly important. For a 12-carbon straight-chain detergent, one has the potential of about -10 kcal/mole favorable free energy change from removal of the alkyl chain into the hemi-micellar state of the adsorbed monolayer.

For fatty acids the dominant terms are still the hydrophobic and electrostatic terms although there is some evidence that specific chemical interaction is occurring between the $-\text{COO}^-$ group and the metal cation in the surface of the mineral. It should be stressed that alternative models, viz., that the metal carboxylate complexes are the active adsorbates or that the surface nucleates a film or coating of metal carboxylate precipitate, have not been eliminated. In testing these various possibilities, several workers have used oleic acid or sodium oleate. Unfortunately, oleate solutions are unstable and it is possible that polymeric or cross-linked oleate species may be the active adsorbate, and one gets the ambiguous appearance of an apparent $\Delta G_{\text{chem}}^\circ$ term [8].

Both fatty acids and the alkylammonium salts exhibit interesting adsorption behavior at pH values around their pK_a and pK_b values, respectively. It appears that the neutral molecule ($\text{R}-\text{COOH}$ or $\text{R}-\text{NH}_2$) is able to lower the $-\text{COO}^-$ or $-\text{NH}_3$ head group-head group repulsion in the adsorbed layer. Marked increases in adsorption are therefore observed as the pH approaches to within 1 unit of the pK_a or pK_b . As the pH moves away from the pK_a or pK_b to make $\text{R}-\text{COOH}$ or $\text{R}-\text{NH}_2$ the predominant species, adsorption decreases sharply since now there is no electrostatic term to localize the molecules so that a significant hydrophobic energy term might act.

In all considerations with long-chain surfactants, marked increases in adsorption occur at about 1/100 of the critical micelle concentration (cmc) of the particular surfactant.

Polymeric s

The principles of polymer and polyelectrolyte adsorption have been the subject of several reviews [9, 10], and will not be discussed in detail here. What will be attempted is to extend the consideration of small organics and organic surfactants to the case of polymer adsorption.

Turning to Eq. (9), viz.,

$$\Delta G_{\text{ads}}^\circ = \Delta G_{\text{elec}}^\circ + \Delta G_{\text{solv}}^\circ + \Delta G_{\text{hb}}^\circ + \Delta G_{\text{vdw}}^\circ + \Delta G_{\text{chem}}^\circ \quad (9)$$

similar considerations apply. Polymers opposite in sign to the surface

are usually more strongly adsorbed and, for example, lead to better flocculation than neutral or polymers of like charge. Similarly, polyelectrolytes are strongly solvated and yet individual singly charged groups or dipoles are not strongly solvated. There seems to be little evidence that specific site-polar group interactions occur, so that $\Delta G_{\text{chem}}^{\circ}$ will tend to be small.

The major interactions are ($\Delta G_{\text{hb}}^{\circ} + \Delta G_{\text{vdw}}^{\circ}$). When the polymer is large and approaching the size of the colloidal particles to which it has been added, significant heterocoagulation will occur, controlled in large part by the dispersion force interaction between the polymer particle and the colloidal (solid) particle. Such systems can exhibit secondary minimum coagulation, and the rheological properties are thereby greatly modified by the presence of polymer.

In discussing hydrophobic effects in polymer adsorption, emphasis must be placed on entropy changes. As one large, hydrated polymer or polyelectrolyte molecule approaches the hydrated surface of a solid, many water molecules must be released to the solution during the adsorption step. This vast increase in the number of kinetic units represents a large positive change in entropy of the system. Thus in

$$\Delta G_{\text{hb}}^{\circ} = \Delta H_{\text{hb}}^{\circ} - T\Delta S_{\text{hb}}^{\circ}$$

since $\Delta S_{\text{hb}}^{\circ}$ is large and positive, then provided $\Delta H_{\text{hb}}^{\circ}$ is also negative or slightly positive one gets an overall $-\Delta G_{\text{hb}}^{\circ}$ for the system. Since the polymer groups themselves are moving from an aquo- to a surface hydroxo-environment in the process of adsorption, it is reasonable to expect that $\Delta H_{\text{hb}}^{\circ}$ is indeed small.

The polymer chain itself may change its conformation upon adsorption, although it need not be significantly more restricted in the adsorbed state. For those polymers that exhibit flocculation effects on dispersions of colloidal solids, which action is considered due to polymer molecules bridging particles together, then the adsorbed polymer may even have a larger radius of gyration when adsorbed. For those polymers which at high surface coverage induce stabilization of colloidal solids, there is definite evidence that the general structure of the polymer is unchanged in the adsorbed state; for such systems the θ -temperature of the bulk polymer in solution is identical to that in the adsorbed state.

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